The discovery of Type-IV binary fluid phase behavior

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ABSTRACT

The analysis by Scott and Van Konynenburg of the binary Van der Waals mixture for constant excluded volume uncovered the Type-IV phase diagram as a transition between Type-II and Type-III phase diagrams. The common boundary of the regions of Type-II and Type-III is a locus of tricritical points. The tricritical locus meets the common boundary of regions of Type-II and Type-IV at what Meijer coined the Van Laar point in 1989. As early as 1905, the Dutch chemist Van Laar had studied the geometric-mean Van der Waals binary mixtures, produced Type-II and Type-III phase diagrams, and found the exact coordinates of what we call the Van Laar point, but he did not notice tricriticality explicitly. He postulated and proved the existence of Type-IV. Aspects of his proof are discussed.

Key words: critical state; history; phase diagrams; Van Laar; Van der Waals binary mixture; vapor-liquid equilibria

## 1. Introduction

In 1890, Van der Waals [1, 2] introduced a generalization of his equation of state to fluid mixtures. The Van der Waals binary mixture equation of state is

$$(P + a_x/V^2)(V - b_x) = RT \tag{1}$$

with $P$ the pressure, $T$ the temperature, $V$ the molar volume, $R$ the molar gas constant, and $x$ the mole fraction of the second component (usually the less volatile one).

The attraction parameter $a_x$ is defined in terms of those of the two components, $a_{11}$, and $a_{22}$, by means of

$$a_x = a_{11}(1 - x)^2 + 2\, a_{12}\, x(1 - x) + a_{22}\, x^2 \tag{2}$$

with $a_{12}$ the mixing parameter. Likewise

$$b_x = b_{11}(1 - x)^2 + 2\, b_{12}\, x(1 - x) + b_{22}\, x^2 \tag{3}$$

Van der Waals's was the first model able to produce phase transitions in binary fluid mixtures, including critical lines, three and four fluid-phase equilibrium, and azeotropy. After early analytic work performed by Korteweg, see [2, 3] and by Van Laar, [4-6], see [2], the model lay dormant until it was resuscitated by Van Konynenburg and Scott beginning in the late 1960s. Their extensive computer-based calculation of phase behavior resulted in a well-known classification of Types-I...V of phase behavior for the Van der Waals binary mixture [7]. They discovered the small region of Type-IV behavior, intermediate between Type II and Type III, and noted that Van Laar, in the early $20^{th}$ century, had calculated the exact coordinates of the point where Types II and III meet. This point was later named the Van Laar point by Meijer [8]. The boundary between Type-III and Type-IV is a locus of tricritical points, where two liquid phases and a vapor phase become identical. The boundary between Type II and Type IV is a locus of double points where a critical line touches a three-phase line. Van Konynenburg and Scott [7] refer to several binary mixtures having Type-IV phase behavior, such as benzene and high-molecular-weight polyisobutylene, first studied by Freeman and Rowlinson in 1960.

This paper focuses on Type-IV, showing that the Dutch chemist Van Laar was the first to postulate Type-IV [4] in 1905, and proved by a computational tour-de-force [6] that it follows from the Van der Waals binary-mixture equation. His discovery of Type IV will be discussed in the context of Meijer's work on the Van Laar point [8, 9].

## 2. Phase behavior of the Van der Waals binary mixture

Three types of phase behavior of the Van der Waals binary mixture are shown in the pressure-temperature diagrams of Fig. 1. Type-II shows a continuous critical line connecting the critical points $C_1$, $C_2$ of the two components. There is a three-phase liquid-liquid-vapor (LLV) split at low temperatures, ending in an upper critical end point $CEP_1$, from where a second critical line (LL) departs for high pressures. Type-III has a critical line near the critical point of the first, more volatile component. This critical line ends at a critical end point $CEP_2$, from where a three-phase LLV curve moves to low pressures. From the critical point $C_2$ of the second, less volatile component, another critical line, which can have a variety of shapes depending on the interactions of the components, ultimately runs to high pressures.
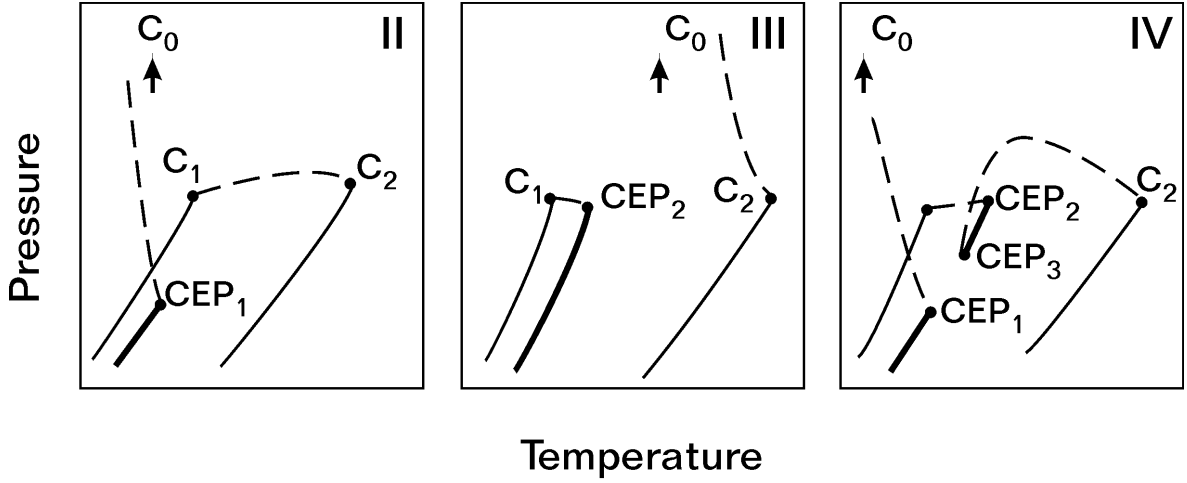
Fig. 1 Types-II, -III, and -IV of binary-mixture fluid phase diagrams in pressure-temperature representation. Full light curves: vapor pressure curves of the two components, with $C_1$, $C_2$ their critical points. $C_0$: mixture critical point at infinite pressure. CEP: critical end point. Heavy curves: three-phase lines liquid-liquid-vapor. Dashed curves: critical lines.

Type-IV, which displays two three-phase regions LLV, three critical end points $CEP_{1-3}$, and three critical lines, forms the transition between Type-II and Type-III. Type-III transforms into Type-IV if, due to a variation of an adjustable parameter in the model, the critical line running to infinite pressure develops a pressure minimum on the way to lower temperatures, and cuts through the three-phase line before moving to high pressures. The part of the critical line between $CEP_1$ and $CEP_3$ is then no longer stable.

Type IV transforms into Type II if an interaction parameter is changed so that the length of the upper three-phase line (LLV) shrinks to zero. This happens by passage through a (asymmetric) tricritical point, at which the two liquid phases and the vapor phase become identical. Even though the phase rule forbids tricriticality from occurring in a two-component mixture, it can happen in the Van der Waals model because an interaction parameter can vary smoothly, unlike molecular parameters of real fluids.

3. The Van der Waals binary mixture around the Van Laar point

Van Konynenburg and Scott represent global fluid phase behavior of the Van der Waals binary mixture for the case of constant excluded volume in terms of two parameters, $\Lambda$ and $\zeta$. The first one, $\Lambda$, is defined as

$$\Lambda = (a_{11} + a_{22} - 2a_{12})/(a_{11} + a_{22}) \qquad (4)$$

The second parameter, $\zeta$, represents the difference of the attraction parameters of the two components:

$$\zeta = \left| a_{11} - a_{22} \right| / (a_{11} + a_{22}) \qquad (5)$$

Types II, III and IV phase behavior all occur for relatively weak attraction between the two components, that is, for positive $\Lambda$. The arrangement of the phases in $\Lambda$, $\zeta$, space, according to Meijer [8], is shown in Fig. 2. This figure is not to scale. In fact, Type-IV

occupies only a very thin sliver of parameter space.  Van Laar was the first to calculate exactly the location of the point where the three regions meet for a version of the Van der Waals model.   Fig. 2 also shows a curve labeled ADP, for "actual double point."  This is the locus of points for which the critical line, dipping down in pressure, just touches the three-phase line before turning up again, thus causing the transition from Type III to Type IV.  In addition, another locus is shown, called MDP, for  "mathematical double point."  The MDP, found by Van Laar, see below, forms on an unstable part of the isothermal Helmholtz energy surface.  Fig. 2 also shows the tricritical locus, which separates the regions of Type II and Type IV.  A variant of Type-IV, named Type IV*, which we will not discuss here, separates Type II and Type III beyond the Van Laar point, see Ref. [7].
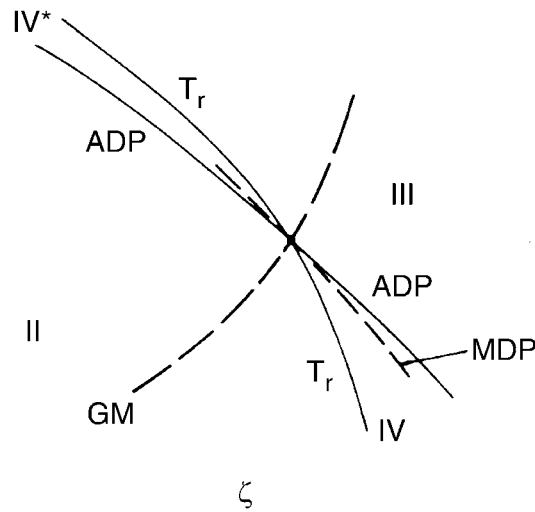


Fig. 2.  Regions of Type-II, -III and -IV phase behavior around the Van Laar point in the plane of two interaction parameters $\Lambda$, $\zeta$, defined in Eqs. 4, 5.  From [2], after Meijer [8]. Tr: locus of tricritical points; MDP: locus of mathematical double points; ADP locus of actual double points; gm: geometric-mean locus.  The plot is not to scale. The region of Type-IV* is a narrow sliver that is easily missed [7].

4.  Van Laar and the geometric-mean Van der Waals binary mixture

In the period of 1905-1907 Van Laar wrote a dozen papers about the phase behavior of the Van der Waals binary mixture.  His interest stemmed from classes he had taken earlier with Van der Waals. Lacking the preparation for a PhD study, however, he was, at that time, an unpaid lecturer of theoretical chemistry at the University of Amsterdam, repeatedly passed over for a more secure position.

In most, but not all, of Van Laar's work, the excluded volume $b_x$ is taken to be a constant independent of $x$. Van Laar limited his calculations exclusively to the case for which the attraction parameter $a_{12}$ of the mixture is the geometric mean of those of the two components

$$a_{12} = (a_{11}.a_{22})^{1/2} \tag{6}$$

In the parameter space of Fig. 2, the geometric-mean locus is indicated as a dotted curve, which happens to pass through the meeting point of the three types of phase behavior, a lucky coincidence indeed.

Van Laar [4] began his analysis of the Van der Waals geometric-mean binary mixture by deriving an exact relationship for the so-called spinodal, with $b_x$ assumed to be a linear function of $x$. The spinodal is the locus of points on the isothermal Helmholtz energy $A(V, x)$ surface at which the curvature turns from positive to negative (thermodynamically unstable). The spinodal is relatively easy to calculate, since it follows from a local condition on the surface, contrary to phase boundary, which requires a search for two phases fulfilling the Gibbs conditions of phase equilibrium. Van Laar's expression for the spinodal is linear in temperature, quadratic in composition, and cubic in volume. Van Laar's next step [5] was to find the critical point on each of the isothermal spinodals for the case of constant excluded volume. In the left column of Fig. 3, we show Van Laar's graphs, for three different choices of $\varphi \equiv a_{11}^{1/2}/(a_{22}^{1/2} - a_{11}^{1/2})$, of a succession of such isothermal spinodals in the $V$-$x$ diagram, labeled by their respective reduced temperatures. Fig. 3 also shows the projection of the critical curve for two choices of $\varphi$, and for $b$ not depending on $x$. The close-packed volume is at the top, and the critical volume at the bottom. The case marked $\varphi = 1$ corresponds to $a_{11}/a_{22} = 1/4$, a large difference in volatility of the two components. In that case, the critical points of the two components, $C_1$ and $C_2$, are not connected. $C_1$ connects with A, at zero temperature and close packing. $C_2$ connects with $C_0$, at finite temperature and close packing, and therefore infinite pressure.

The case marked $\varphi = 2$ corresponds to $a_{11}/a_{22} = 4/9$, the difference in volatility small enough for the critical line to connect $C_1$ and $C_2$, while A connects with $C_0$. The bottom figure will be discussed in Sec. 5.

Van Laar gave an exact expression for the coordinates $T$, $x$, $V$ of the point, at which the connectivity of the two critical-line loci switches. This expression was quoted in Ref. [7] and confirmed by means of symbolic computation by Meijer et al. [9]. In the right column of Fig. 3, we show Van Laar's corresponding $P$-$T$ diagrams. To avoid confusion, we use the designations of the types as introduced by Scott and used throughout this paper, rather than the different ones used by Van Laar. The $\varphi = 2$ case represents a Type-II phase diagram, and the $\varphi = 1$ a Type-III one.

The Van Laar $P$-$T$ plots, however, are not the same as the similar-looking plots in Fig. 1. Since Van Laar did not calculate coexistent phases, his plots only show critical lines, but not any three-phase regions. Thus, the points $R_1$ and $R_2$ in Fig. 3 are not critical end points, but cusps in the critical line, which occur on an unstable part of the Helmholtz energy surface. In the $V$-$x$ diagram, it is seen that the critical line touches an isothermal spinodal at this particular temperature and thus must reverse its course in temperature. Van Laar [6] proved that in the $P$-$T$ diagram this happens by passage through a cusp.

5

Volume

Composition

Pressure
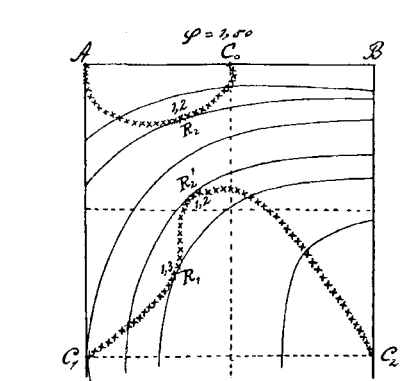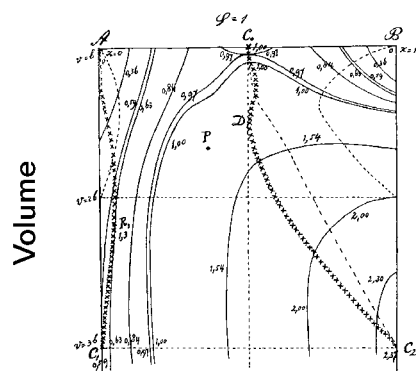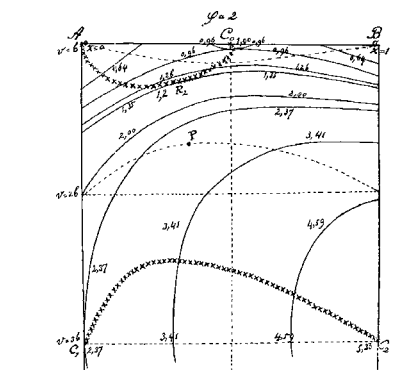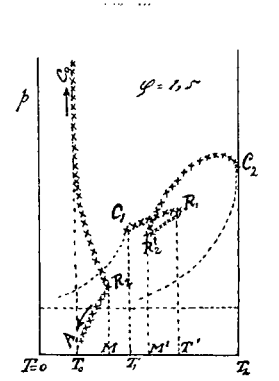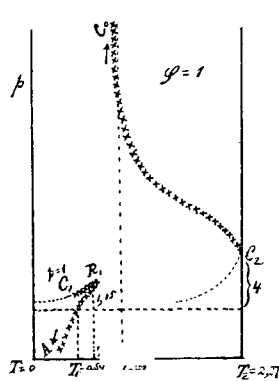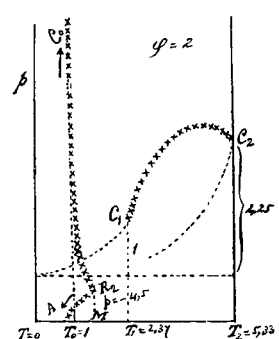
Temperature

Fig. 3. The top row ($\varphi = 2$) corresponds with Type-II, middle row ($\varphi = 1$) with Type-III, and bottom row ($\varphi = 1.5$) with Type-IV phase behavior of the Van der Waals binary mixture. The top and middle row are calculated accurately, the bottom row is hypothesized. From Van Laar in 1905 [5]. Left column: isothermal spinodals ———— labeled with the reduced temperature, and critical lines xxxxx are shown in the volume-composition plane. Close-packing is at the top, the critical volume at the bottom. $C_0$, $C_1$ and $C_2$ as in Fig. 1. "A" indicates the critical point at close packing and at $T = 0$. Right column: Critical lines xxxxx, as well as vapor pressure curves ———— of the pure components, are indicated in the *P-T* diagram.

5. Van Laar postulates and proves the existence of Type-IV

Van Laar [5] speculated that, in general, the transition from Type II to Type III must take place through a new type of phase diagram, which is shown in the bottom row of Fig. 3. In *P-T* coordinates (right), it looks much like Type IV, but again we must remember that only critical lines are shown. The parts of the critical lines around cusps in critical lines are located on unstable parts of the Helmholtz energy surface. The critical line A-$C_0$, running to high pressures, touches a spinodal once, in $R_2$. The critical line connecting $C_1$ and $C_2$, however, touches two spinodals, and thus has two cusps, $R_1$ and $R_2'$. Type IV turns into Type II when, on varying a parameter of the model smoothly, $R_1$ and $R_2'$ are made to coincide at an inflection point in the *V-x* projection of the critical line. Type IV turns into Type III when, on varying a model parameter, $R_2$ and $R_2'$ are made to coincide at a mathematical double point on the critical line, after which the connectivity of the critical lines switches, as discussed in Sec. 4.

The intrepid Van Laar then set out to prove that his conjecture, the critical line connecting $C_1$ and $C_2$ touching two isothermal spinodals in the *V-x* plane and thus forming a new type of phase diagram, follows from the geometric-mean Van der Waals equation [6]. First of all, he worked through the case for constant excluded volume. Perhaps not surprisingly, he found, after lengthy calculations, that this is a pathological case, the two touching points $R_1$ and $R_2'$ coinciding at what is presently called the Van Laar point. Undaunted, Van Laar then turned to another case of the Van der Waals geometric-mean binary mixture, a case he had studied before, in which not the excluded volumes, but the reduced critical pressures of the two components are equal. This implies that $a_{11}/b_{11}^2 = a_{22}/b_{22}^2$. It turned out that the switch of connectivity of the critical lines for this case occurs for *x* as small as 0.01, at close packing $V = b_x$, and for a ratio of the critical temperatures of the components close to 10. Van Laar showed that for a substantial range of reduced temperatures the critical line connecting $C_1$ and $C_2$ touches two spinodals. He calculated that the transition from Type II to Type IV occurs for a critical temperature ratio $T_{c2}/T_{c1} = 4.44$, and for the transition from Type IV to Type III for $T_{c2}/T_{c1} = 9.90$. Van Laar presented these extensive calculations in a 50-page paper, one of many he wrote within a few years' time on related topics.

6. Discussion

For Van Laar, the truly remarkable phenomenon is the exchange of connectivity of the critical lines (Fig. 3). This marks the end of Type III, and the transition to Type II (at the Van Laar point), or, in general, to Type IV (below the Van Laar point in Fig. 2). This transition happens when, in the Type III $P$-$T$ diagram, the critical line running from $C_2$ to $C_0$ touches the critical line running from $C_1$ to A in an MDP, after which two new cusps are formed, the critical points $R_2'$ and $R_1$ in Fig. 3, bottom right. From the viewpoint of Van Konynenburg and Scott, (Fig. 1), who limited themselves to the thermodynamically stable regions, the critical line from $C_2$ to $C_0$ becomes unstable after it touches and then cuts the three-phase line in an ADP, that is, before it reaches the MDP. By focusing on the mathematical description, Van Laar defines the boundary between Type-III and Type-IV in one way. By focusing on thermodynamic stability, Van Konynenburg and Scott define the boundary differently.

　　　As to the transition from Type-II to Type-IV, Van Laar focuses on the coalescence of the cusps $R_1$ and $R_2'$, in an unstable region, through an inflection point on the projection of the critical line on the $V$-$x$ plane. Scott and Van Konynenburg, on the other hand, focus on the disappearance of a three-phase line in the stable region, and are thus led to the phenomenon of tricriticality, to the study of which Scott and coworkers afterwards made major contributions. The resulting Type-II to Type-IV boundary, however, is the same in both cases.

　　　As the history of the discovery of Type-IV phase equilibrium illustrates, the knowledge of mixture phase diagrams by the Dutch school around 1900 was deep and extensive, notwithstanding the lack of computational tools. Much of the early theoretical knowledge has been gradually rediscovered after computers became available.

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